

PATENT ABSTRACTS OF JAPAN

(11)Publication number : **2000-095577**
(43)Date of publication of application : **04.04.2000**

(51)Int.Cl.

C04B 35/71

A61K 6/033

A61L 27/00

C04B 35/447

C04B 35/80

(21)Application number : **10-287275**

(71)Applicant : **ASAHI OPTICAL CO LTD**

(22)Date of filing : **24.09.1998**

(72)Inventor : **HIRAIDE TSUNEO**

KUBOTA YUKIO

MIYAKE SHOTARO

(54) PRODUCTION OF HYDROXYAPATITE-METAL COMPOSITE AND HYDROXYAPATITE-METAL COMPOSITE

(57)Abstract:

PROBLEM TO BE SOLVED: To produce a hydroxyapatite-metal composite excellent in affinity for a living body and having safety and stability in water and satisfactory mechanical strength and to provide its producing method.

SOLUTION: When a hydroxyapatite and a metallic material are combined by a discharge plasma sintering method to produce a hydroxyapatite-metal composite, the hydroxyapatite is previously subjected to temporary sintering. This temporary sintering is preferably carried out at 700-1,300°C and discharge plasma sintering is more preferably carried out at $\leq 600^{\circ}\text{C}$ sintering temp. The metallic material is preferably titanium or its alloy.

CLAIMS

[Claim(s)]

[Claim 1]A manufacturing method of a hydroxyapatite metal complex carrying out the temporary-quenching join of said hydroxyapatite beforehand in a manufacturing method of a hydroxyapatite metal complex which composite-izes hydroxyapatite and a metallic material by discharge plasma sintering.

[Claim 2]A manufacturing method of the hydroxyapatite metal complex according to claim 1 in which said temporary-quenching join is performed at temperature of 700-1300 **

[Claim 3]A manufacturing method of the hydroxyapatite metal complex according to claim 1 or 2 in which said discharge plasma sintering is performed below at temperature

of said temporary-quenching join.

[Claim 4]A manufacturing method of the hydroxyapatite metal complex according to any one of claims 1 to 3 which performs discharge plasma sintering at sintering temperature of 600 ** or less using said hydroxyapatite which carried out the temporary-quenching join at temperature of 700-1300 **.

[Claim 5]A manufacturing method of the hydroxyapatite metal complex according to claim 4 which performs discharge plasma sintering at sintering temperature of 550 ** or less using said hydroxyapatite which carried out the temporary-quenching join at temperature of 700-1000 ** (except for 1000 **).

[Claim 6]A manufacturing method of the hydroxyapatite metal complex according to any one of claims 1 to 5 which performs said temporary-quenching join under atmosphere near ordinary pressure.

[Claim 7]A manufacturing method of the hydroxyapatite metal complex according to any one of claims 1 to 6 which performs said temporary-quenching join under oxygen existence atmosphere.

[Claim 8]A manufacturing method of the hydroxyapatite metal complex according to any one of claims 1 to 7 which consists of a mixed material containing said hydroxyapatite and said metallic material.

[Claim 9]A manufacturing method of the hydroxyapatite metal complex according to claim 8 whose weight ratios of said hydroxyapatite and said metallic material of said mixed material are 1 / 20 - 1/1.

[Claim 10]A manufacturing method of the hydroxyapatite metal complex according to any one of claims 1 to 9 in which said metallic material is titanium or a titanium system alloy.

[Claim 11]A manufacturing method of the hydroxyapatite metal complex according to any one of claims 1 to 10 which cancels and cools radiationally a pressurization state after said discharge plasma sintering.

[Claim 12]A hydroxyapatite metal complex manufacturing by a method according to any one of claims 1 to 11.

[Claim 13]The hydroxyapatite metal complex according to claim 12 used as a biomechanical material.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which an invention belongs] This invention relates to the hydroxyapatite metal complex manufactured by manufacturing method of the hydroxyapatite metal complex excellent in the manufacturing method of a hydroxyapatite metal complex especially intensity and biocompatibility, and safety, and a manufacturing method for the same.

[0002]

[Description of the Prior Art] Hydroxyapatite has the biocompatibility which was excellent since the structure of the bony mineral constituent was resembled, and is applied as biomechanical materials, such as a dental implant, a bone filler, dental cement. However, a mechanical strength, toughness of hydroxyapatite, etc. were not enough and there was a limit in use with a hydroxyapatite independent.

[0003]Then, in order to obtain the biomechanical material which fully has a mechanical strength, toughness, etc., it is tough and the method of composite-izing the metallic material which is excellent in a moldability, and hydroxyapatite with a sintering process, etc. are proposed, for example.

[0004]For example, in discharge plasma sintering, in order to control oxidation, deterioration, etc. of die materials and a sintered material, sintering is usually performed under a vacuum or an inert gas atmosphere.

[0005]However, if a metallic material and hydroxyapatite are simultaneously sintered under a vacuum or an inert gas atmosphere, An oxidation-reduction reaction arises between a metallic material and hydroxyapatite, and while a metallic material combines with oxygen in hydroxyapatite and oxidizes, the phenomenon in which the oxygen atom in hydroxyapatite is taken by the metallic material may arise. There was a problem that the presentation, crystal structure, etc. changed, the hydroxyapatite from which the oxygen atom was taken served as an unstable substance that it is easy to collapse, and it became difficult to form a good complex with a metallic material.

[0006]When the complex containing the hydroxyapatite collapsed or disassembled was immersed underwater, the decomposition product of hydroxyapatite, such as a calcium oxide, was eluted and there was a problem that the pH value of immersion fluid rose.

[0007]

[Problem(s) to be Solved by the Invention]There is the purpose of this invention in providing the hydroxyapatite metal complex manufactured by the manufacturing method and this manufacturing method of a hydroxyapatite metal complex provided with safety and stability a sufficient mechanical strength and underwater while it is excellent in biocompatibility.

[0008]

[Means for Solving the Problem]Such a purpose is attained by this invention of following the (1) - (13).

[0009](1) A manufacturing method of a hydroxyapatite metal complex carrying out the temporary-quenching join of said hydroxyapatite beforehand in a manufacturing method of a hydroxyapatite metal complex which composite-izes hydroxyapatite and a metallic material by discharge plasma sintering.

[0010](2) A manufacturing method of a hydroxyapatite metal complex given in the above (1) to which said temporary-quenching join is performed at temperature of 700-1300 **.

[0011](3) A manufacturing method of a hydroxyapatite metal complex the above (1) to which said discharge plasma sintering is performed below at temperature of said temporary-quenching join, or given in (2).

[0012](4) A manufacturing method of a hydroxyapatite metal complex the above (1) which performs discharge plasma sintering at sintering temperature of 600 ** or less using said hydroxyapatite which carried out the temporary-quenching join at temperature of 700-1300 ** thru/or given in either of (3).

[0013](5) A manufacturing method of a hydroxyapatite metal complex given in the above (4) which performs discharge plasma sintering at sintering temperature of 550 ** or less using said hydroxyapatite which carried out the temporary-quenching join at temperature of 700-1000 ** (except for 1000 **).

[0014](6) A manufacturing method of a hydroxyapatite metal complex the above (1) which performs said temporary-quenching join under atmosphere near ordinary pressure

thru/or given in either of (5).

[0015](7) A manufacturing method of a hydroxyapatite metal complex the above (1) which performs said temporary-quenching join under oxygen existence atmosphere thru/or given in either of (6).

[0016](8) A manufacturing method of a hydroxyapatite metal complex the above (1) which consists of a mixed material containing said hydroxyapatite and said metallic material thru/or given in either of (7).

[0017](9) A manufacturing method of a hydroxyapatite metal complex given in the above (8) whose weight ratios of said hydroxyapatite and said metallic material of said mixed material are 1 / 20 - 1/1.

[0018](10) A manufacturing method of a hydroxyapatite metal complex the above (1) in which said metallic material is titanium or a titanium system alloy thru/or given in either of (9).

[0019](11) A manufacturing method of a hydroxyapatite metal complex the above (1) which cancels and cools radiationally a pressurization state after said discharge plasma sintering thru/or given in either of (10).

[0020](12) A hydroxyapatite metal complex manufacturing by a method the above (1) thru/or given in either of (11).

[0021](13) A hydroxyapatite metal complex given in the above (12) used as a biomechanical material.

[0022]

[Embodyment of the Invention]Hereafter, the hydroxyapatite metal complex manufactured by manufacturing method of the hydroxyapatite metal complex of this invention and a method for the same is explained in detail.

[0023]The manufacturing method of the hydroxyapatite metal complex (henceforth a "complex") of this invention composite-izes hydroxyapatite and a metallic material by discharge plasma sintering, and carries out the temporary-quenching join of said hydroxyapatite beforehand.

[0024]Since the degree of crystallinity of hydroxyapatite becomes large and activity falls by performing such a temporary-quenching join, reductive disassembly of hydroxyapatite by a reaction with a metallic material can be controlled in the case of discharge plasma sintering.

[0025]As for the temporary-quenching join of hydroxyapatite, it is preferred to be carried out at the temperature of 700-1300 **. The activity of hydroxyapatite cannot fully be reduced as temporary-quenching join temperature is less than 700 **, A reaction with metal may be unable to be inhibited at the time of sintering, and there is fear, like on the other hand, if it exceeds 1300 **, hydroxyapatite will decompose thermally, or it becomes difficult for grain growth to advance superfluously and to form a complex with a metallic material good.

[0026]Although the temporary-quenching join of the hydroxyapatite performed in order to acquire the above-mentioned effect is not limited in particular for the pressure in a temporary-quenching join, it is preferred to carry out near ordinary pressure. About a sintered atmosphere, it is preferred to carry out, for example under the air middle class and oxygen existence atmosphere, for example, a temporary-quenching join can be performed using an air furnace.

[0027]Although the hydroxyapatite used for the manufacturing method of the complex of

this invention may be powder state or it may be a block body, when it is a granular material, as for the mean particle diameter, it is preferred that it is about 1-500 micrometers, and its about 10-400 micrometers are more preferred.

[0028]The hydro-KIAPA tight metal complex in particular manufactured by the manufacturing method of this invention may not be limited for the shape, structure, etc., but may be what kind of thing. For example, the complex which the layer which is mainly concerned with hydroxyapatite, and the layer which is mainly concerned with a metallic material laminate, the complex which consists of a mixed material containing hydroxyapatite and a metallic material, etc. are mentioned.

[0029]When using the mixed material containing hydroxyapatite and a metallic material, it is preferred that the weight ratios of hydroxyapatite in a mixed material and a metallic material are 1 / 20 - 1/1.

[0030]When the above-mentioned weight ratio is smaller than 1/20, the rate of hydroxyapatite is small, there is a possibility that the biocompatibility of a complex may be spoiled, and the feature as bioceramics may become is hard to be revealed. On the other hand, if larger than 1/1, the rate of a metallic material is small and improvement in a mechanical strength, etc. may not fully be attained.

[0031]That is, the complex which reveals notably the biocompatibility of hydroxyapatite, the desirable characteristic of both who are called the high intensity which a metallic material has, and a function can be obtained by making the weight ratio of hydroxyapatite and a metallic material into this range.

[0032]Although not limited especially as a metallic material, it is preferred to use metal with small noxiousness, For example, although Ti, Cr, Fe, Co, Cu, Mo, Ag, Au, nickel, Pd, Pt, aluminum, Nd, Sn, Zr, etc. are mentioned and these can be used combining one sort or two sorts or more, Ti (titanium) or a titanium system alloy is especially more preferred. Titanium is excellent in corrosion resistance, and its noxiousness is very small, and since a metal ion is hardly eluted underwater and in body fluid, it excels especially as a biomechanical material.

[0033]A "titanium system alloy" here means the alloy which is mainly concerned with titanium. Although not limited especially as metallic elements other than the titanium which constitutes this titanium system alloy, it excels in corrosion resistance, and a thing safe for a living body is preferred, for example, the above metallic elements are mentioned, and these can be used combining one sort or two sorts or more. As for the content of metallic elements other than titanium in a titanium system alloy, it is preferred that it is about 5-20wt%.

[0034]A metallic material may be powder state, or may be a block body, and, as for the mean particle diameter, in the case of a granular material, it is preferred that it is about 20-200 micrometers.

[0035]The mixed material can mix and prepare hydroxyapatite and the metallic material which performed the temporary-quenching join using a mortar etc. In addition, as a mixer which can be used, a ball mill, a rod mill, a double coat blender, a V shaped rotary mixer, etc. are mentioned, for example.

[0036]Hydroxyapatite and a metallic material may be mixed and distributed uniformly and the mixture ratio of a mixed material is good also as an inclination material which changes continuously or gradually.

[0037]As mentioned above, with a metallic material, the hydroxyapatite by which the

temporary-quenching join was carried out is sintered by discharge plasma sintering, and is composite-ized.

[0038]Discharge plasma sintering supplies pulse form direct electrical energy to a green compact particle gap, is applying effectively the high energy of the high-temperature plasma generated in an instant by spark discharge to thermal diffusion, electrolysis diffusion, etc., and enables sintering / composite-ization including temperature up and retention time in about 5 to 20 minutes.

[0039]According to such discharge plasma sintering, for example like hydroxyapatite and a metallic material, sintering temperature and intensity are greatly different, it is a short time and the complex in which composite-ization was made difficult until now can be manufactured high-definition.

[0040]Porosity sintering made usually difficult can be performed easily, and the complex which was suitable as a biomechanical material can be manufactured.

[0041]Drawing 1 is drawing of longitudinal section showing the principal part of the discharge-plasma-sintering device used for the manufacturing method of this invention.

[0042]The forming die 1 has the shape of a cartridge which has the material insertion part 11, and one pair of forming punches 2 which fit into both ends slidably are arranged.

[0043]As a component of the forming die 1 and the forming punch 2, conductive materials, such as superhard metal, cemented carbide, and carbon system materials (black lead, glassy carbon, etc.), are used, for example. Such a forming die 1 is filled up with the mixed material 4 containing hydroxyapatite and a metallic material as shown in drawing 1.

[0044]Each of inner skin of the forming die 1 and press surfaces of the forming punch 2 is covered with the carbon sheet 5. Thereby, the forming punch 2 can be slid smoothly, without biting the inner circumference of the forming die 1. Since the ingredient in the mixed material 4 may react to the carbon contained in the forming die 1 or the forming punch 2, said ingredient can be prevented from adhering to an internal surface etc. by making the carbon sheet 5 intervene.

[0045]Drawing 2 is drawing of longitudinal section showing other examples of the principal part of the discharge-plasma-sintering device used for the manufacturing method of this invention.

[0046]In this case, concentric circle shape is filled up with the metallic material 4b which becomes the material insertion part 11 of the forming die 1 from the hydroxyapatite 4a, titanium, or a titanium system alloy. It is constituted so that the hydroxyapatite 4a and the metallic material 4b may be separately pressed with the forming punch 2a and 2b.

[0047]Thus, when filling up and sintering so that the hydroxyapatite 4a and the metallic material 4b may become concentric circle shape, it can equalize about the temperature and pressure distribution in the direction (diameter direction) which intersects perpendicularly with a pressurizing direction, and it becomes possible to produce the complex excellent in intensity.

[0048]Discharge plasma sintering inserts the above-mentioned mixed material 4 of the specified quantity in the forming die 1, sandwiches it with the forming punch 2, is set in the discharge-plasma-sintering device 70 as shown in drawing 3, and is performed.

[0049]The discharge-plasma-sintering device 70 is provided with the following.
Vacuum chamber 76.

The pressurizing rams 74 and 75 of an up-and-down couple.

The power supply 72 for sintering which generates pulse voltage.

The hydraulic application-of-pressure drive mechanism 73 which carries out the rise-and-fall drive of the pressurizing rams 74 and 75, and the control section 71 which controls these.

[0050]The forming die 1 which inserted in the mixed material 4 mentioned above is set between the pressurizing rams 74 and 75 in the vacuum chamber 76.

[0051]The inside of the vacuum chamber 76 is deaerated by the vacuum pump 77, and let it be a vacua (reduced pressure state). Since discharge plasma sintering has a possibility of oxygen in the air, nitrogen, water, etc. reacting to the reactant high ingredient etc. which are contained in the mixed material 4, and having the influence which is not preferred on a complex, it is preferred to sinter the inside of the vacuum chamber 76 by a vacua (reduced pressure state) or an inert gas atmosphere beforehand.

[0052]The control section 71 controls the output of the power supply 72 for sintering so that the material temperature detected by the thermo sensor (thermo couple) which was installed in the forming die 1, and which is not illustrated is in agreement with the temperature-up curve set up beforehand. The control section 71 controls the drive of the application-of-pressure drive mechanism 73 and the vacuum pump 77.

[0053]It is being respectively fixed to the pressurizing rams 74 and 75, and the forming punch 2 of the up-and-down couple is electrically connected with the power supply 72 for sintering by the power supply terminal (not shown) provided in the pressurizing ram 74 and 75.

[0054]By the operation of the application-of-pressure drive mechanism 73, the pressurizing rams 74 and 75 are moved in the direction which approaches mutually, and the mixed material 4 is compressed with the forming punch 2 fixed to these.

[0055]Although the welding pressure in particular at the time of compression is not limited, a 100 - 600kgf/cm² grade is preferred, and a 200 - 500kgf/cm² grade is more preferred. When welding pressure is too small, there is a possibility that the compactness and intensity of a sintered compact may become insufficient. Manufacturing efficiency falls -- sintering time becomes long. On the other hand, if welding pressure is too large, the resistance to pressure of the forming die 1, etc. will pose a problem.

[0056]It sinters by compressing the mixed material 4, carrying out the seal of approval of the pulse voltage through the forming punch 2, and energizing pulse current.

[0057]The conditions in particular of the pulse voltage to impress are not limited, for example, a pulse ratio (deenergization time: resistance welding time) can make them 1:1 to about 12:1, and about voltage 1-10V.

[0058]Although the sintering temperature in discharge plasma sintering is suitably set up with a kind, abundance, etc. of a metallic material, it is preferred to be carried out below at the temperature of the temporary-quenching join of hydroxyapatite. When sintering temperature exceeds temporary-quenching join temperature, an oxidation-reduction reaction occurs between hydroxyapatite and a metallic material, and hydroxyapatite has a possibility of oxygen in a molecule being taken with a metallic material, and carrying out reduction decomposition. As a result, when the decomposition product of hydroxyapatite, such as a calcium oxide and phosphine, is included in a complex and such a complex contacts water, body fluid, etc., there is a problem of these decomposition products harmful to a human body being eluted to water, body fluid, etc., or a pH value rising

greatly.

[0059]As for the sintering temperature in discharge plasma sintering, it is preferred to consider it as 600 ** or less, when the temporary-quenching join of hydroxyapatite is performed at 700-1300 **, and when temporary-quenching join temperature is 700-1000 ** (except for 1000 **), it is still more preferred to consider it as 550 ** or less.

[0060]Thus, by considering temporary-quenching join temperature and sintering temperature in discharge plasma sintering as such a relation, the rise of the pH value of the water by decomposition of the above-mentioned problem, i.e., hydroxyapatite, and the decomposition product of hydroxyapatite, body fluid, etc. can be prevented.

[0061]According to the manufacturing method of this invention, since a hydroxyapatite metal complex can be manufactured by low temperature sintering 600 ** or less, thermal disassembly of the hydroxyapatite produced in a sintering process can be controlled effectively.

[0062]As for the retention time in the sintering temperature mentioned above, about 2 to 30 minutes is preferred, and it is more preferred. [of about 5 to 15 minutes] By considering it as the sintering time of this range, fault sintering of a sintered material, etc. can be prevented and it can be considered as the complex excellent in intensity.

[0063]After carrying out predetermined time maintenance at sintering temperature, gradual cooling is carried out and a sintered compact (complex) is taken out from the forming die 1.

[0064]In the case of gradual cooling, it is preferred to cancel a pressurization state and to cool a sintered compact radiationally. In the usual method of water-cooling a sintered compact via a forming punch etc., while maintaining a pressurization state, there is a possibility that the crack and chip by heat stress may occur, like the combination of hydroxyapatite and a metallic material in the complex which consists of material with a large difference of a coefficient of thermal expansion. Therefore, it is preferred to cancel and cool a pressurization state radiationally in this invention.

[0065]As for the hydroxyapatite metal complex of this invention manufactured as mentioned above, being used as a biomechanical material is preferred.

[0066]The complex of this invention makes hydroxyapatite excellent in biocompatibility, and the metallic material which is excellent in intensity, toughness, and processability composite-ize, and the characteristic which was excellent in both is revealed.

[0067]It fully has impact strength and toughness with biocompatibility, and in body fluid, it can be stable, and a toxic substance cannot be eluted, but the complex using very small titanium or the titanium system alloy of noxiousness especially as a metallic material can be operated safely in the living body.

[0068]As a biomechanical material in which the complex of this invention may be applied, an artificial bone, a dental implant, an artificial joint, bone supplementation material, etc. are mentioned, for example.

[0069]As mentioned above, although the hydroxyapatite metal complex manufactured by manufacturing method of the hydroxyapatite metal complex of this invention and a method for the same was explained using figures, This invention is not limited to this and other ingredients, for example, ceramics materials other than hydroxyapatite, etc., may be contained in the complex.

[0070]

[Example]Next, concrete working example of this invention is described.

[0071]1. Production of hydroxyapatite metal complex (working example 1)

[0072]2.8 g of titanium granular materials (mean particle diameter: 25 micrometers) were mixed with 0.7 g of spherical hydroxyapatite granular materials (mean particle diameter: 80 micrometers) which carried out the temporary-quenching joint at 1200 ** using the air furnace as a metallic material, and the mixed material 4 (HAp/Ti ratio = 1/4) was prepared.

[0073]This mixed material 4 was inserted in the forming die 1 as shown in drawing 1, and it allocated so that it might insert with the forming punch 2 which becomes those upper and lower sides from the conductive carbon of a couple. The inner skin of the forming die 1 and the press surface of the forming punch 2 were covered with the carbon sheet 5.

[0074]Next, it sets in a discharge-plasma-sintering device (Sumitomo Coal Mining Co., Ltd. make SPS-510L) as shows drawing 3 the forming die 1 and the forming punch 2, It pressurized by 350kgf/cm² from the upper and lower sides in the vacuum, and the seal of approval of the pulse voltage (pulse condition-12:2) was carried out, the compression energization system was heated, and it sintered in sintering temperature [of 550 **], and retention time 10 minutes.

[0075]Then, the pressurization state was canceled and the sintered compact was cooled radiationally under the room temperature. The presentation of a mixed material, the particle diameter of each material, a sintering condition, etc. are shown in Table 1.

[0076]

[Table 1]

表 1

	材料重量 [g]		HAp/Ti 重量比		粒径 [μm]		板焼結温度 [$^{\circ}\text{C}$]		焼結温度 [$^{\circ}\text{C}$]		加圧力 [kgf/cm 2]		保持時間 [分]
実施例 1	0. 70	2. 80	1/4	8.0	2.5	1200	650	350	550	950	350	350	1.0
実施例 2	0. 70	2. 80	1/4	8.0	2.5	1100	550	350	550	950	350	350	1.0
実施例 3	0. 70	2. 80	1/4	8.0	9.0	1000	550	350	550	950	350	350	1.0
実施例 4	0. 70	2. 80	1/4	8.0	2.5	900	550	350	550	950	350	350	1.0
実施例 5	0. 70	2. 80	1/4	8.0	2.5	1200	600	600	600	600	350	350	1.0
実施例 6	0. 70	2. 80	1/4	8.0	9.0	1100	600	600	600	600	350	350	1.0
実施例 7	0. 70	2. 80	1/4	8.0	2.5	1050	600	600	600	600	350	350	1.0
実施例 8	0. 15	3. 00	1/20	8.0	2.5	1300	600	600	600	600	350	350	1.0
実施例 9	1. 25	1. 25	1/1	8.0	9.0	700	650	650	650	650	350	350	1.0
実施例 10	1. 25	1. 25	1/1	150	2.5	1200	650	650	650	650	400	400	1.0
実施例 11	1. 00	2. 00	1/2	4.00	9.0	1100	550	550	550	550	350	350	1.0
比較例 1	0. 70	2. 80	1/4	8.0	2.5	板焼結せず [†]	550	550	550	550	350	350	1.0
比較例 2	0. 70	2. 80	1/4	8.0	9.0	板焼結せず [†]	950	950	950	950	350	350	1.0
比較例 3	0. 90	2. 10	3/7	1.0	2.5	板焼結せず [†]	900	900	900	900	350	350	1.0

1) : HAp …ハイドロキシアパタイト

[0077](Working example 2) The complex was produced like working example 1 except the temporary-quenching join temperature of hydroxyapatite having been 1100 **.

[0078](Working example 3) The temporary-quenching join temperature of hydroxyapatite was 1000 **, and the complex was produced like working example 1 except having changed the mean particle diameter of titanium.

[0079](Working example 4) The complex was produced like working example 1 except the temporary-quenching join temperature of hydroxyapatite having been 900 **.

[0080](Working example 5) The complex was produced like working example 1 except the sintering temperature of discharge plasma sintering having been 600 **.

[0081](Working example 6) The sintering temperature of discharge plasma sintering was

600 **, and the complex was produced like working example 2 except having changed the mean particle diameter of titanium.

[0082](Working example 7) Temporary-quenching join temperature was 1050 **, and the complex was produced like working example 6 except having changed the mean particle diameter of titanium.

[0083](Working example 8) The presentation of the mixed material was changed and the complex was produced like working example 5 except the temperature of the temporary-quenching join having been 1300 **.

[0084](Working example 9) The presentation of the mixed material was changed and the complex was produced like working example 3 except the temperature of the temporary-quenching join having been 700 **.

[0085](Working example 10) The complex was produced like working example 1 except having changed the presentation of a mixed material, the particle diameter of hydroxyapatite, and the welding pressure at the time of sintering.

[0086](Working example 11) The complex was produced like working example 1 except having changed the particle diameter and sintering temperature of the presentation of a mixed material, hydroxyapatite, and titanium powder.

[0087](Comparative example 1) The complex was produced like working example 1 except having used the hydroxyapatite which does not perform a temporary-quenching join.

[0088](Comparative example 2) The complex was produced like working example 1 using the hydroxyapatite which does not perform a temporary-quenching join except having changed the particle diameter of titanium powder, and sintering temperature.

[0089](Comparative example 3) The complex was produced like working example 1 using the hydroxyapatite which does not perform a temporary-quenching join except having changed the particle diameter and sintering temperature of the presentation of a mixed material, and hydroxyapatite.

[0090]2. After picking out the complex produced by quality evaluation working example 1-11 and the comparative examples 1-3 of the complex from the type for shaping, the carbon sheet was removed, and the grinder removed the contact surface with the carbon sheet on the surface of a complex further.

[0091]After being immersed for three days under the room temperature into about 20-times the amount pure water of complex weight in this state, the pH value of immersion fluid was measured in hydrogen ion exponent meter.

[0092]This immersion fluid was diluted with pure water 5 times after immersing a complex, and the content of the calcium contained in this diluent was measured. Measurement was performed using the high frequency plasma-emission-spectrometry device.

[0093]The state of the complex after being immersed for three days was observed visually, and the existence of the collapse phenomenon was checked. These results are shown in Table 2.

[0094]

[Table 2]

表 2

	浸漬液中 カルシウム濃度 [ppm] ²⁾	浸漬液 pH	崩壊現象
実施例 1	0. 47	7. 2	無
実施例 2	0. 45	7. 3	無
実施例 3	0. 48	7. 3	無
実施例 4	0. 68	7. 4	無
実施例 5	0. 90	7. 1	無
実施例 6	0. 85	7. 5	無
実施例 7	0. 69	7. 6	無
実施例 8	0. 42	7. 1	無
実施例 9	0. 90	7. 6	無
実施例 10	0. 47	7. 2	無
実施例 11	0. 45	7. 3	無
比較例 1	35. 10	11. 6	有
比較例 2	39. 00	12. 1	有
比較例 3	37. 50	12. 0	有

2) : 5 倍希釈液中の濃度

[0095]As for each of each complexes produced in working example, from the result of Table 2, hydroxyapatite and titanium were composite-ized homogeneously, and even if this complex was immersed in pure water for three days, neither the rise of the pH value of immersion fluid nor the collapse phenomenon of the complex was seen. Most calcium was not detected out of immersion fluid (5 time diluent).

[0096]On the other hand, since the complex produced by each comparative example did not perform the temporary-quenching join of hydroxyapatite, during discharge plasma sintering, hydroxyapatite and titanium reacted and hydroxyapatite disassembled it. For this reason, when a complex was immersed in pure water for three days, high-concentration calcium was detected out of immersion fluid (inside of a diluent).

[0097]The decomposition product of hydroxyapatite, such as a calcium oxide and phosphine, was eluted to immersion fluid, and the pH value of immersion fluid rose remarkably. The immersion fluid alkalinity-ized according to elution of the decomposition product made disassembly of hydroxyapatite accelerated further, and the complex has collapsed in immersion fluid.

[0098]

[Effect of the Invention]As stated above, according to the manufacturing method of the hydroxyapatite metal complex of this invention, the complex which dissimilar materials composite-ized good by the simple method can be manufactured.

[0099]Disassembly of hydroxyapatite under discharge plasma sintering can be controlled by carrying out the temporary-quenching join of the hydroxyapatite. For this reason, there is no complex manufactured by the method of this invention about a harmful decomposition product being eluted underwater etc. or the complex itself collapsing, and it excels in underwater safety and stability.

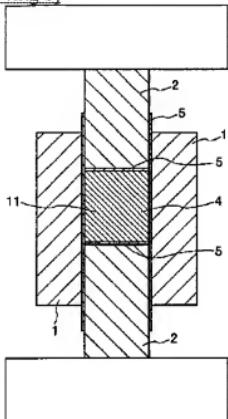
[0100]The complex of this invention is provided with the characteristic of both hydroxyapatite and a metallic material.

It has biocompatibility and excels in intensity and toughness.

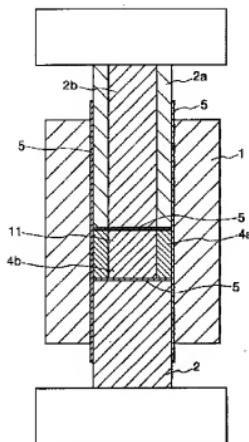
[0101]Therefore, taking advantage of such the characteristic, it is widely applicable as biomechanical materials used when an intervertebral disk is excised in a cervical vertebra or lumbar vertebrae, such as bone supplementation material, a dental implant, an artificial bone, and an artificial joint.

DRAWINGS

[Drawing 1]



[Drawing 2]



[Drawing 3]

